

The University of Chicago

I. ADDITIONS OF HALOGEN ACIDS
TO OLEFINIC COMPOUNDS

II. SOME DERIVATIVES OF HIGHER
BENZENE HOMOLOGUES

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1939

By

JAMES A. NORTON

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James Allan Norton

Chicago, Illinois
December, 1939

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CHAPTER I

THE ADDITION OF HYDROGEN BROMIDE TO TRICHLOROETHYLENE

Introduction

Previous investigations¹ have demonstrated that the "normal" addition of hydrogen bromide to halogenated ethylenes and propylenes (vinyl chloride, 1-chloropropene, etc.) proceeds at a very much slower rate than addition to the corresponding alkenes. However, in spite of the fact that the peroxide-catalyzed "abnormal" addition of the halogen ethylenes is rapid, it has been possible to effect a "normal" addition under strictly antioxidant conditions. Thus, in the case of vinyl chloride, 60 to 70 per cent of the 1,1-isomer was obtained in fourteen days, depending upon the antioxidant used. It appeared probable, therefore, that if the substitution of hydrogen atoms by halogen atoms decreases the rate of "normal" addition, the "normal" addition in the case of trichloroethylene would become very slow, and that the result of the reaction would be the peroxide-catalyzed addition product. The expectations concerning the slowness of the "normal" reaction were realized. The reaction is so slow that I could find no uncatalyzed "normal" addition of hydrogen bromide to trichloroethylene. Furthermore, I was able to adduce addition evidence that the presence of two hydrogen atoms on the terminal carbon atoms of the double bond is not an essential structural feature for molecules which exhibit a "peroxide effect."

Previous Work

There appears to be no previous record of the addition of hydrogen bromide to trichloroethylene. Hydrogen chloride has been added to this compound in the presence of aluminum chloride

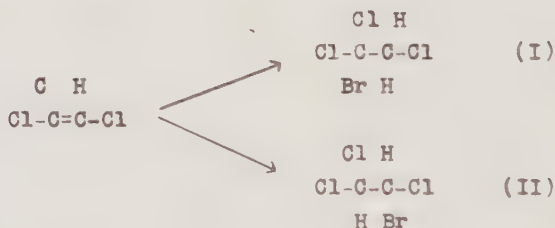
¹See Kharasch, Engelmann, and Mayo, J. Org. Chem., 2, 288 (1937) for references.

by Prins,¹ who obtained unsymmetrical tetrachloroethane in the temperature range 30-40°. With the same catalyst, Müller and Hönn² used somewhat higher temperatures and obtained other products as well as unsymmetrical tetrachloroethane, probably via halogen interchange.

1,1,2-Trichloro-1-bromoethane is not described in the literature. Van de Walle³ describes 1,1,2-trichloro-2-bromoethane, and submits proof for its structure and that of the third possible isomer of the same empirical formula, 1,1,1-trichloro-2-bromoethane.

Discussion of Results

From considerations of structure, it appears that hydrogen bromide could add to trichloroethylene to give either 1,1,2-trichloro-1-bromoethane (I) or 1,1,2-trichloro-2-bromoethane (II):



Upon the basis of the hypothesis previously advanced,^{4,5} the unsymmetrical tetrahalide (I) should be the "normal" addition product while the symmetrical tetrahalide (II) should be the "abnormal" addition product, and the latter should be formed in the presence of oxygen and/or peroxides.

Table 1 shows the inability to detect any addition of hydrogen bromide to trichloroethylene under "antioxidant"

¹Prins, Rec. trav. chim., **45**, 80 (1926).

²Müller and Hönn, J. prakt. Chem., **133**, 289 (1932).

³Van de Walle, Bull. soc. chim. Belg., **28**, 304 (1914).

⁴Kharasch and Darkis, Chem. Rev., **5**, 571 (1928).

⁵Kharasch and Reinmuth, J. Chem. Ed., **8**, 1703 (1931).

TABLE 1

ADDITION OF HYDROGEN BROMIDE AND HYDROGEN CHLORIDE TO TRICHLOROETHYLENE
IN THE ABSENCE OF AIR AND PEROXIDES

Moles ^a HBr	Added Substances	Moles ^a Adden- dum	Illumination	Reaction ^b Time, Days	Addition (Per cent)	Remarks
1.30	Ph ₂ NH	.015	None	60	0	
1.30	Ph ₂ NH	.015	Sunlight	30	0	
2.15	EtSH	.031	None	60	0	
1.65	PhSH	.038	None	60	0	
1.37	t-Bu-N=C	.022	None	60	0	
1.63	PhSH	.030	Pyrex Hg arc	0.83	0	
1.81	t-Bu-N=C	.079				
	AcOH	2.19				
	EtSH	.067	None	60	0	
1.46	AcOH	.715	None	60	0	
1.58	PhSH	.030	None	2 (100°)	0	
1.55	AcOH	.909	None	1	73	Addition product exclusively
1.55	PhSH	.054	None	1	81	1,1,2-trichloro-1-bromo-
1.15	FeCl ₃	.005	None	1 (0°)	35	ethane (I)
1.85	FeCl ₃	.004	None	1	--	Inseparable mixture
1.85	AlCl ₃	.005	None			
1.50	AlCl ₃	.006	None			
Moles ^a HCl						
1.57	FeCl ₃	.003	None	6	49	Addition product exclusively
1.62	AlCl ₃	.004	None	3 (0°)	22	1,1,1,2-tetrachloroethane

^aCalculated on basis of trichloroethylene used.

^bReactions were carried out at room temperature except as noted.

TABLE 2

ADDITION OF HYDROGEN BROMIDE TO TRICHLOROETHYLENE IN THE PRESENCE OF AIR^c AND/OR PEROXIDES

Moles ^a HBr	Peroxides ^a Moles	Illumination	Total Ron. Time, Hrs.	Yield ^{a,d} Add. Prod.	Remarks
1.50	None	None	60 x 24	0	
1.50	Bz ₂ O ₂ .024	None	17	2	
1.74	Bz ₂ O ₂ .099	None	120	5	Bz ₂ O ₂ added at 4 daily intervals
1.81	Bz ₂ O ₂ .110	None	24	27	
2.63	Bz ₂ O ₂ .207	None	48	1	
1.50	Bz ₂ O ₂ .004	None	24	3	Bz ₂ O ₂ added to HBr- C ₂ HCl ₃ mixture just before sealing
1.50	Bz ₂ O ₂ .004	None	24	1.2	Bz ₂ O ₂ added to C ₂ HCl ₃ just before adding HBr
1.57	Bz ₂ O ₂ .010	Sunlight, 3 hrs.	3'	57	
1.50	Bz ₂ O ₂ .004	None	24	0.8	Solution of Bz ₂ O ₂ in C ₂ HCl ₃ stood 25 hrs. before adding HBr
1.10	Ascar. .025	Sunlight, 5 hrs.	5	1	Peroxide destroyed very rapidly
1.50	None	Pyrex Hg aro, 3 1/2 hrs.	3 1/2	6	
1.50	Bz ₂ O ₂ .004	Pyrex Hg aro, 3 1/2 hrs.	3 1/2	30	
1.50	None	Sunlight, 8 hrs.	27	91	
1.50	Bz ₂ O ₂ .004	Sunlight, 9 hrs.	27	89	
1.50	Bz ₂ O ₂ .004	Sunlight, 9 hrs.	27	90	Air excludcd

^{a, b} Have same significance as in Table 1.^c All runs in presence of air except one experiment as noted.^d Product exclusively 1,1,2-trichloro-2-bromoethane.

conditions, even after thirty days in sunlight or when the reaction mixture was heated to 100° for two days. In a number of cases, the reaction mixture was kept for two months in the dark without showing any signs of addition.

The slowness of the "normal" addition is also shown by results which were obtained in the attempted addition of hydrogen iodide to trichloroethylene. Hydrogen iodide is the halogen acid which adds most readily to ethylene bonds. An equimolar mixture of the two showed only a faint iodine color and no volume change after four days' standing in darkness in the absence of air at room temperature. The iodine color was comparable to that given by hydrogen iodide alone in a few weeks under such conditions. When a similar mixture was exposed to sunlight for two weeks, 25 per cent of the trichloroethylene was reduced to 1,1,2-trichloroethane and a large quantity of iodine separated. There was no evidence of any product boiling higher than trichloroethane. It is concluded that no appreciable addition of hydrogen iodide took place in the dark, and that if any addition took place in the light the product was quickly reduced by hydrogen iodide.

Table 1 shows that, as might be anticipated from the results of Kharasch, Engelmann, and Mayo,¹ ferric chloride catalyzes the "normal" addition of hydrogen bromide to trichloroethylene. Yields of over 80 per cent of the unsymmetrical tetrahalide (I) were obtained by use of a few thousandths of a mole of ferric chloride. The reaction requires several hours at room temperature. The same result was obtained with aluminum chloride at 0° , but with yields of only 30-40 per cent. The poor yield is attributed not to inferiority of aluminum chloride as a catalyst, but rather to its slight solubility in the reaction mixture. At room temperature, in the presence of aluminum chloride, part of the excess hydrogen bromide reacts with the addition product to give hydrogen chloride and a complex mixture of boiling range $90-200^{\circ}$ at 20 mm. No definite fractions were isolable on the Podbielniak² column.

To substantiate the belief that the compound formed in the presence of the chlorides of aluminum or iron was the

¹Kharasch, Engelmann, and Mayo, J. Org. Chem., 2, 288 (1937).

²Podbielniak, Ind. Eng. Chem., Anal. Ed., 5, 119 (1933).

unsymmetrical tetrahalide (I), addition of hydrogen chloride to trichloroethylene in the presence of ferric chloride was tried, since a "peroxide effect" has never been observed with this hydrogen halide. The addition proceeded slowly at room temperature to give unsymmetrical tetrachloroethane exclusively. Aluminum chloride at 0° gave the same results, corroborating Prins¹ results at room temperature.

Table 2 records the results of experiments made in the presence of air or peroxides. Ascaridole was found to decompose rapidly in a reaction mixture, with the result that the mixture became opaque and only slight addition took place. Benzoyl peroxide was found to be soluble in the reaction mixture and to cause the development of little or no color on standing. The results show that in the presence of air and in darkness, no addition takes place unless a peroxide is added and that even then the reaction is extremely slow. When the reaction is carried out in the light (sunlight or mercury arc), either air or added peroxide will accelerate the reaction. The product was always exclusively 1,1,2-trichloro-2-bromoethane.

Comparable experiments with mercury arc illumination indicate that the reaction is faster in the presence of both air and peroxides than in the presence of air alone. Another experiment in sunlight shows that peroxides catalyze the addition in the absence of air. That air alone is as effective as peroxides alone in sunlight is readily explainable. Oxygen in the light can furnish small amounts of peroxide over a long period while benzoyl peroxide may be destroyed slowly under the conditions of the experiment.

The proof of structure of the two possible addition products (I) and (II) is given in the Experimental Part.

Experimental Part

Trichloroethylene.—Trichloroethylene was obtained from the Eastman Kodak Company, and after suitable purification a constant-boiling fraction was collected and used. The trichloroethylene used in this work was stabilized with diphenylamine. Any desired quantity of the pure reagent was obtained by simple distillation

¹Prins, Rec. trav. chim., 45, 80 (1926).

from stock.

Technique.--Experiments were made either in the presence or absence of air according to the procedure of Kharasch and Mayo.¹ After the bombs had stood for the desired length of time, they were cooled to -80° and opened. Excess hydrogen bromide was removed by shaking and warming to room temperature. Since the progress of the addition could be estimated by noting the change in the volume of the contents of the bomb, the procedure of analysis adopted when little or no change in volume was observed was to transfer the residue in the bomb tube to a small distilling apparatus and to note the boiling range. Usually the temperature of the vapor did not rise above 90° , except when certain added materials were present. If the volume change during the course of the addition was significant, the bomb contents were distilled in vacuo on the Podbielniak column² at a pressure of 20-22 mm. A trap was used to recover any unchanged trichloroethylene. The fractions collected had a boiling range of 0.2° or less. After distillation, the index of refraction was determined.

Identification of addition products.--Table 3 summarizes the physical constants of the addition products obtained, and determinations of the molecular weights and halogen contents of the hydrogen bromide addition products. Halogen determinations were made according to the method of Vaughn and Nieuwland³ and Fajans.

Proof of structure.--Compound (I) was treated with zinc in hot alcohol. The product was unsymmetrical dichloroethylene. This was confirmed by treatment with chlorine and identification of the resulting unsymmetrical tetrachloroethane (yield from [I], 52 per cent) by boiling point and index of refraction.

Since 1,1,1-trichloro-2-bromoethane gives the same product with zinc in hot alcohol, hydrolysis of (I) with alcoholic sodium phenate was carried out. The product was trichloroethylene in 60 per cent yield. This product was identified by boiling point and index of refraction, and also by addition of

¹Kharasch and Mayo, J. Am. Chem. Soc., **55**, 2468 (1933).

²Podbielniak, Ind. Eng. Chem., Anal. Ed., **5**, 119 (1933).

³Vaughn and Nieuwland, Ind. Eng. Chem., Anal. Ed. **3**, 274 (1931).

TABLE 3

PHYSICAL CONSTANTS OF ADDITION COMPOUNDS OF TRICHLOROETHYLENE

Property	$\text{Cl}_2\text{BrC}-\text{CH}_2\text{Cl}$	$\text{Cl}_2\text{CH}-\text{CHClBr}$	$\text{Cl}_2\text{BrC}-\text{CHClBr}$	$\text{Cl}_2\text{C}-\text{CH}_2\text{Cl}$	$\text{Cl}_2\text{CH}-\text{CHCl}_2$
B.P. 760	152°	171° (172°) ^a	204° (dec.) 116.5°	129° (130°) ^b	144.5° (145.0°) ^b
B.P. 50	54.0°	68.9°			
B.P. 20	1.5217	1.5302	1.5710	1.4828 (1.4821) ^c	1.4947 (1.4951) ^d
n_D^{20}					
$n_D^{14.5}$					
Mol. wt. in benzene (cryoscopic)	206.2 (calculated 212.3)	198.9, 201.9 (calculated 212.3)			
% Halogen calc'd as Cl^- for volumetric analysis	66.67 66.91 66.56 (calculated 66.71)	66.62 66.59 66.62 (calculated 66.71)			

^aVan de Walle, Bull. soc. chim. Belg., 28, 304 (1914).^b"International Critical Tables," McGraw-Hill Book Co., New York, 1928, 3, 216.^cHenne and Hubbard, J. Am. Chem. Soc., 58, 404-406 (1936).^dEckart, Brennstoff-Chem., 4, 24-5 (1923); Chem. Abstr., 17, 2356 (1923).

bromine. The identity of the bromine addition product was confirmed by boiling point. By similar treatment, (II) also gave trichloroethylene.

Compound (II) was likewise treated with zinc in hot alcohol. The products were the cis- and trans- symmetrical dichloroethylenes. When these were treated with chlorine, symmetrical tetrachloroethane (yield, 69 per cent) was obtained, identified by boiling point and index of refraction.

Summary

1. In the presence of anhydrous ferric or aluminum chloride, hydrogen bromide adds to trichloroethylene to give 1,1,2-trichloro-1-bromoethane, which is not formed in the absence of such catalysts.

2. In the presence of air and benzoyl peroxide, hydrogen bromide adds very slowly to trichloroethylene to give 1,1,2-trichloro-2-bromoethane. The formation of this product is markedly accelerated by light in the presence of either air or added peroxides.

3. Physical constants and proof of structure for the above compounds are given. Boiling points and indices of refraction are also given for the tetrachloroethanes and for 1,1,2-trichloro-1,2-dibromoethane.

CHAPTER II

THE ADDITION OF HYDROGEN IODIDE TO OLEFINIC COMPOUNDS

This study was undertaken in an effort to explain the results obtained by Ingold and Ramsden¹ in their addition of hydrogen iodide to propene, and of Kharasch and Hannum² in their addition of hydrogen iodide to allyl bromide.

A number of workers have studied the addition of hydrogen iodide to propene.^{1,2,3} The consensus of opinion is that the sole product of the reaction is isopropyl iodide. Ingold and Ramsden, however, claimed to have obtained up to 25 per cent of n-propyl iodide in some of their addition products. Thus, the pure reactants alone gave about 24 per cent n-propyl iodide; and in propane, a typical non-polar solvent, 25 per cent of n-propyl iodide was obtained. Relatively non-polar solvents gave the best yields of n-propyl iodide. Relatively polar solvents, such as nitrobenzene, acetic acid, and water gave less n-propyl iodide than the pure reactants alone. The method of addition consisted in breaking a sealed tube of propene within a sealed tube of hydrogen iodide (and solvent, if any) at a temperature of $18^{\circ} \pm 2^{\circ}$, which was maintained throughout the course of the reaction. The solvent effect is claimed by Ingold and Ramsden to vary with the "mean molecular fraction of hydrogen iodide in its mixture with the solvent (if any) during the course of the reaction." Unfortunately, their paper fails to give the following pertinent information: whether air was excluded from the reaction vessel; whether any iodine was formed during the course of the reaction;

¹Ingold and Ramsden, J. Chem. Soc. (1931) 2743.

²Kharasch and Hannum, J. Am. Chem. Soc., 56, 1782 (1934).

³(a) Berthelot, Ann., 104, 184 (1857); (b) Erlenmeyer, ibid., 139, 228 (1866); (c) Butlerov, ibid., 145, 275 (1867); (d) Markovnikov, ibid., 153, 256 (1869); (e) Michael and Leighton, J. prakt. Chem., (2) 60, 445 (1899); (f) Emschwiller, Ann. chim., (5) 17, 500 (1932).

how much propene was used in the solvent-hydrogen iodide mixture and how much of it was isolated as addition product; how the "mean molecular fraction of hydrogen iodide" was calculated; and how long any individual experiment was allowed to proceed.

Kharasch and Hannum¹ record that with propene, allyl bromide, 1-butene, neopentylethylene, and vinyl chloride, they obtained isopropyl iodide, 1-bromo-2-iodopropane, 2-iodobutane, 2,2-dimethyl-4-iodopentane, and ethylidene chloriodide respectively as the exclusive products of addition. In each case, the product formed was independent of the presence or absence of air, antioxidants, solvents, or peroxides. Because allyl bromide did not react readily with hydrogen iodide under "antioxidant" conditions at -33° but did in the presence of ascaridole, they concluded that peroxides accelerate the "normal" addition of hydrogen iodide. They also concluded that the failure to find a "peroxide effect" with hydrogen iodide was due to the rapid destruction of the peroxide by the hydrogen iodide.

A short study was made of the behavior of trichloroethylene with hydrogen iodide. This was discussed earlier in the thesis (p. 5).

The Addition of Hydrogen Iodide to Propene

The product of the addition of hydrogen iodide to propene in all of the experiments recorded in Table 4 was exclusively isopropyl iodide. Michael and Leighton² indicated that a small amount of high-boiling material was formed and reported that n-propyl iodide was one of the constituents to the extent of 0.3 per cent of the total addition product. This was not proved conclusively, however. A similar observation was made in the present work, but the index of refraction of this material was lower than that of isopropyl iodide. Therefore, the main constituent of the residue could not be n-propyl iodide. The amount of this material was too small for definite identification, but it is suspected that it is a hexyl iodide. An experiment in which n-propyl iodide was added to a mixture of pure reactants demonstrated that the failure to find the primary iodide in other experiments was

¹Kharasch and Hannum, J. Am. Chem. Soc., 56, 1782 (1934).

²Michael and Leighton, J. prakt. Chem., (2) 60, 445 (1899).

TABLE 4

THE ADDITION OF HYDROGEN IODIDE TO PROPENE^a

Expt. No.	Moles ^b	Added Substances	Moles ^c	Reaction Time, Hr.	Temp. °C.	Yield, Product (%)	Remarks
113 (1)	1.17	None	----	21	-80	59	Reaction incomplete
74	0.36	None	----	1	0	33	
75	3.51	None	----	1 1/2	0	80	
127 (7)	1.00	None	----	3	0	95	
94	1.02	None	----	1	R.T.	95	Ingold technique
146	1.01	None	----	2 3/4	0	91	Ingold technique
140	1.00	HgI ₂	.015	94 (5 min.)	0	94	
141	1.00	HgI ₂	.013	10 min. (5 min.)	0	95	
147	1.00	Hg (mirror)	.04	2 3/4 (1/2)	0	96	
102	1.11	Air	----	2	R.T.	92	
42	1.31	Air	----	1/2	-10	74	Ingold technique
133	1.00	Air	----	3	0	94	
142	1.00	Powdered Pyrex	0.5 gr.	2 1/2	0	90	Reaction homogeneous
89 ^b (1)	1.14	Ascaridole	.005	3 min. (1 min.)	-80	92	Overheated
50	1.12	Ascaridole, air	.005	2 1/2	-80	85	HI run in during 2 hrs.
88	1.09	I ₂	.005	3 min. (1 min.)	-80	93	Overheated
87	1.11	H ₂ O	.05	1	R.T.	94	
112	1.16	H ₂ O	.05	1 1/3	0	91	No catalytic effect noted
128 (2)	1.00	H ₂ O	.05	2 1/4	0	91	
134	1.00	CH ₃ -CH ₂ -CH ₂ I	.34	16	R.T.	98	All n-PrI recovered
106 ^c	1.81	CH ₃ -CH ₂ -CH ₂ I	1.00	14	R.T.	--	98 per cent recovery of n-PrI
98	1.09	C ₃ H ₈	.78	25	R.T.	95	Ingold technique
105	1.09	C ₃ H ₈	2.44	15	R.T.	94	
49	1.09	C ₅ H ₁₂	.66	46 1/4	R.T.	92	
139	0.81	C ₅ H ₁₂	2.94		R.T.	67	

TABLE 4--CONTINUED

Expt. No.	Moles ^c	Added Substances	Moles ^c	Reaction Time, Hr.	Temp. °C. ^e	Yield Product (%)	Remarks
52 ^h	1.41	Ascaridole, C ₅ H ₁₂ , & air	.010 1.10	2 1/2	-80	33	Propene lost during slow introduction of HI
90 (1)	1.05	CH ₃ COOH	.87	24	R.T.	94	Solvent not dried
63	1.00	C ₂ H ₅ SH	.27	4	0	59	Thioethers formed
76	0.78	C ₆ H ₅ NO ₂	.55	11 days	R.T.	43	Solvent reduced
143	0.99	(C ₆ H ₅) ₂ NH	.005	2 1/2	0	95	
54	0.11	Ascaridole & HBr	.004 1.02	12	0	66	Iso-PrBr. No n-PrBr.

^aExcept as noted, all experiments were carried out with carefully dried materials in the absence of air and light using the techniques described in the Experimental Part. Usually 5.0 gm. of propene were used. In Experiments 74 and 134, 15 gm. of propene were used.

^bNumbers in parentheses indicate the number of duplicating experiments.

^cBased on ethylene derivative used. Yields on basis described in Experimental Part.

^dNumbers in parentheses indicate time for substantially complete reaction as estimated by volume change.

^e"R.T." indicates room temperature without cooling bath. Bombs may have overheated.

^fAscaridole added intermittently.

^gNo propene used in this experiment. HI quantity based on n-propyl iodide.

^hHI gas passed slowly into mixture for two hours in the presence of air. The ascaridole was added intermittently in several portions.

not due to its instability under these conditions.

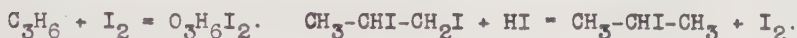
When prepared, the reaction mixtures were colorless and usually only a very faint iodine color developed during the reaction. When much propane was used as solvent, no color developed. If peroxides or iodine had been used in such an experiment, the products were deeply iodine-colored.

An equimolecular mixture of propene and hydrogen iodide was found to require about two hours for 99 per cent reaction at 0° . Mercuric iodide was an effective catalyst for the addition, for in its presence the addition was 100 per cent complete in less than ten minutes at 0° . Added peroxides or added iodine caused addition to take place with almost explosive violence so that the addition was complete in from fifteen to ninety seconds at -80° . The rate of reaction is apparently dependent upon the concentration of dissolved iodine, which in turn is dependent upon the state of subdivision of the solid iodine and the temperature of the reaction mixture. At the same temperature (-80°) in the absence of iodine, the reaction required twenty-four hours for two-thirds completion. The addition was homogeneous in the absence of solvents and catalysts (experiment 142). Water had no effect upon the reaction except to retard the later stages of the reaction if a comparatively large quantity of water had been used. Solvents such as propane or pentane decreased the rate of addition in approximate proportion to the dilution of each reactant, while acetic acid did not make a substantial change in the amount of time required for the complete reaction. The presence of air resulted in some iodine color in the reaction product, but during the time required for the addition the amount of iodine formed was very small. However, iodine continued to be formed after the completion of the addition.

Since the reaction of hydrogen iodide with a peroxide must yield iodine as one of the products, the accelerating effect of peroxides is explained easily. The following evidence suggests that peroxides are immediately and quantitatively destroyed by hydrogen iodide and that the latter serves as an excellent antioxidant for hydrogen bromide additions: The last experiment in Table 4 shows that a slight excess of hydrogen iodide with respect to added ascaridole will prevent any "abnormal" addition of hydrogen bromide to propene. A more striking experiment, not recorded in a table, was carried out with vinyl chloride and

hydrogen bromide to which a small amount of ascaridole and slightly more hydrogen iodide had been added. After a month at room temperature, a 38 per cent yield of the "normal" addition product, ethylidene chlorobromide, was obtained, together with much unreacted material. No ethylene chlorobromide was found. Kharasch and Hannum¹ obtained the "normal" addition product with hydrogen bromide only in the presence of ferric chloride or good antioxidants; otherwise the product was ethylene chlorobromide.

A possible explanation of the catalysis by iodine of the addition of hydrogen iodide to unsaturated compounds such as propene is that propene diiodide is reduced by hydrogen iodide to isopropyl iodide and iodine with explosive violence:²



Ingold and Ramsden³ used nitrobenzene as a solvent in certain of their experiments. As noted by Baumhauer,⁴ concentrated hydriodic acid reduces nitrobenzene to aniline at 100°. Hydrochloric and hydrobromic acids yield di- and trihaloanilines at more elevated temperatures. Experiments in the course of the present work showed that anhydrous hydrogen iodide will reduce nitrobenzene at room temperature; and that when propene was introduced into such a mixture, the yield of isopropyl iodide was only 45 per cent (experiment 76, Table 4) and a quantity of crystalline substituted ammonium iodide separated. Ingold and Ramsden mention no such results.

When all the above experiments had given no indication of the formation of n-propyl iodide, as reported by Ingold and Ramsden, a few experiments were performed using their technique (as nearly as it could be ascertained from their paper) in bringing the reactants to room temperature before mixing. Table 4 lists four such experiments, which were so chosen as to give the highest yield of n-propyl iodide according to Ingold and Ramsden.

¹Kharasch and Hannum, J. Am. Chem. Soc., 56, 712 (1934).

²Malbot, Ann. chim., (6) 19, 355 (1890).

³Ingold and Ramsden, J. Chem. Soc. (1931) 2746.

⁴Baumhauer, Ann. Supp., 7, 208 (1870).

Only isopropyl iodide was found. I am unable, therefore, either to repeat or to explain the formation of the 20-25 per cent of n-propyl iodide which they record.

The Addition of Hydrogen Iodide to Allyl Bromide

The addition of hydrogen iodide to allyl bromide (Table 5) yielded only 1-bromo-2-iodopropane. This addition differs from the corresponding addition to propene in that considerable reduction occurs if the addition is conducted at the ordinary temperature. Observation of the volume changes of reaction mixtures indicate that there is first an induction period lasting about an hour at 0° or 36 to 48 hours at -33°, during which little or no addition takes place, but during which time iodine is slowly liberated. As iodine accumulates, the addition reaction commences and becomes more and more rapid, overtaking the reduction reaction. Hence it is difficult to state with any degree of precision the exact period of time occupied by the induction period. A likely mechanism for the reduction reaction is a halogen exchange with the formation of allyl iodide which is easily reduced by hydrogen iodide. Because of the slowness of the iodine formation and the stability of 1-bromo-2-iodopropane towards hydrogen iodide (experiment 60, Table 5), it seems likely that it is the allyl iodide that is reduced rather than allyl bromide or the addition product. It is claimed by Malbot¹ and Simpson² that allyl iodide is reduced to isopropyl iodide by hydrogen iodide and that 1,2-diiodopropane (propene diiodide) is formed by reaction of equimolar quantities of allyl iodide and hydrogen iodide.

The catalysis by iodine is probably analogous to that in the addition of hydrogen iodide by propene. 1,2-Diiodo-3-bromopropane, formed by the addition of iodine to allyl bromide, is not known in the pure state and is probably too unstable to exist except in equilibrium with allyl bromide and iodine. Its transitory existence, however, is sufficient to explain the iodine catalysis of this addition. It may be assumed that 1,2-diiodo-3-bromopropane is immediately reduced by hydrogen iodide to give iodine and the "normal" addition product, 1-bromo-2-iodopropane.

¹Malbot, Ann. chim., (6) 19, 355 (1890).

²Simpson, Ann., 129, 127 (1864).

TABLE 5

THE ADDITION OF HYDROGEN IODIDE TO ALLYL BROMIDE^a

Expt. No.	Moles ^b HI		Moles ^c	Reaction Time	Temp. ^e	Yield, % Addition Product	Low-boiling Fraction	Remarks
116	1.07	None	----	21	-80	No reaction		
108	1.03	None	----	70	-33	67	35 ^f	
109	1.02	None	----	2	1/2	87	8	
96	1.02	None ^g	----	4	0	87	23	
55	1.09	None	----	24	0	93	7	
57	1.06	Ascaridole	.022	2	10	51	30	
66	1.10	Ascaridole	.014	1	0	36	45	
73	1.11	Ascaridole	.007	1	0	55	44	HBr found in low-boiling fraction
71	1.07	Ascaridole	.014	2	0	93	4 ^b	
64	0.87	Ascaridole	.011	1/3	R.T.	57	42 ^b	Light from Pyrex Hg arc
120	1.07	Ascaridole	.014	19	-35	29	58 ^b	HI run in during 20 minutes
121	1.30	Ascaridole	.088	1/3	20	87	9 ^b	
115	1.00	C ₅ H ₁₂	.01	1/12	0	10	-- ^f	
65	1.13	I ₂	.014	1	0	67	28 ^f	
56	0.91	I ₂	.005	2	0	89	10	
117	1.06	I ₂	.014	47	1/2	70	25	
119	1.10	I ₂ (g)	.014	27	1/2	68	28 ^f	
122	1.12	I ₂	.014	1/12	-33	96	1	
62	0.95	H ₂ O	.06	1	1/2	78	19 ^f	Mixture overheated
97	1.05	H ₂ O (g)	.06	24	0	85	9	Rapid formation of I ₂
118	1.06	H ₂ O	.06	18	-80	85	5	
				70	-33	No reaction	18	

TABLE 5--CONTINUED

Expt. No.	Moles ^b HI	Added Substances	Moles ^c	Reaction Time	Temp. ^e	Yield, % Addition Product	Low-boiling Fraction	Remarks
110	1.01	H ₂ S (g)	1.00	3	0	83	7	
58	1.00	Ph ₂ NH	.007	2 1/2	0	56	40	
69	1.05	Ph ₂ NH	.007	1/2	0	90	6	
60	1.47	I ₂ CH ₃ -CHI-CH ₂ Br	1.00	1	0	92	1	No allyl bromide used. The recovery is listed under "yield"

^{a, c, e} Have the same significance as in Table 4; 10 gm. of peroxide-free (except as noted) allyl bromide was usually used.

^b Special high vacuum distillation for separation of ascaridole decomposition products from addition product as described in Experimental Part.

^d This is the weight of the isopropyl halide-allyl bromide fraction multiplied by 100 and divided by the weight of allyl bromide used.

^f Allyl bromide found in low-boiling fraction. This does not mean that it was absent in others not thus indicated.

^g Allyl bromide gave a positive peroxide test.

TABLE 6
THE ADDITION OF HYDROGEN IODIDE TO ALLYL CHLORIDE^a

Expt. No.	Moles ^c HI	Added Substances	Moles ^c	Reaction Time (Hr.)	Reaction Temp. (°C.) ^e	Yield Addition ^c Product, %	Low-boiling ^d Fraction	Millimoles ^c I ₂ Produced
114	1.09	None	-----	18	0	100	7	Not determined
159	1.24	None	-----	24	0	84	7	3.00
165	1.13	None	-----	52	0	94	6	3.54
167	1.14	None	-----	52	0	93	4	3.77
70	1.10	None	-----	16	R.T.	99	9	Not determined
161	1.23	I ₂ ^b	.00156	5 1/2	0	87	16	7.83
168	1.13	I ₂	.00448	52	0	95	4	6.97
170	1.14	I ₂	.00447	5 3/4	0	93	4	2.20
171	1.13	I ₂	.00447	5 3/4	0	91	4	0.85
169	1.14	H ₂ O	.06	6 1/2	0	92	7	27.65
160	1.11	H ₂ O	.06	12	0	91	7	26.73
156	1.13	HgI ₂	.011	20 1/4	0	87	6	8.06
166	1.13	HgI ₂	.008	52	0	95	0.9	4.95
144	1.05	Reduced Fe	.19	18	-33	86 _f	--	Not determined
157	1.15	Reduced Fe	.27	2	R.T.	4	35	10.68

^{a, c, d, e} Have the same significance as in Table 5; 7.65 gm. (0.100 mole) of allyl chloride usually was used. The moles of iodine were calculated as I₂ rather than as I.

^b Trace of water also present, due to technique employed. Causes high values for iodine produced in reaction.

^f After fractionation. Large amount of tar in the distilling bulb.

^c Urushibara and Takebayashi, Bull. Chem. Soc. Japan, 11, 692 (1936) and succeeding papers, found that reduced iron initiated an abnormal^W addition of hydrogen bromide to allyl bromide.

This last substance was previously mentioned as being stable towards hydrogen iodide at 0° . The amount of iodine formed during the addition was not determined since the "normal" addition product liberates iodine slowly under the influence of air and/or light. Such determinations, which bear out the conclusions above, were made with allyl chloride.

The reduction products were isolated as isopropyl bromide and iodide. There was no indication of the formation of n-propyl halides. The isopropyl halides contained varying amounts of allyl bromide and hence the quantities of low-boiling materials obtained in a given experiment are not a reliable index of the extent of the reduction.

The Addition of Hydrogen Iodide to Allyl Chloride

The addition of hydrogen iodide to allyl chloride exhibits many of the phenomena attendant upon the corresponding addition with allyl bromide. The chloride is, however, more resistant to reduction, and insufficient low-boiling materials were obtained for analysis by fractionation. The induction period at 0° is about twelve hours instead of the one hour as in allyl bromide additions. During these twelve hours, little or no addition takes place, unless iodine or peroxides have been added to the reaction mixture. The amount of iodine formed by reduction depends on the initial iodine concentration (the more iodine, the shorter the induction period, and hence the smaller the extent of the reduction and the amount of iodine formed) and upon the temperature of the reaction mixture. In order to obtain consistent results in the amount of iodine formed during the reaction, it is highly important to keep the gas phase at the same temperature as the liquid phase.

In contrast to the propene-hydrogen iodide addition, mercuric iodide had very little effect on the allyl chloride addition. The rate was about $1\frac{1}{2}$ times that of a pure hydrogen iodide-allyl chloride mixture. Reduction was increased in about the same proportion and the main effect was to shorten the induction period by a few hours.

Water was found to have a strong catalytic effect on the reduction reaction (experiments 160 and 169), probably because it promoted halogen interchange between the allyl chloride and hydrogen iodide. The amount of iodine formed was several times

that formed in a similar experiment conducted under anhydrous conditions. By analogy with the addition of hydrogen iodide to propene, it is believed that water exerts no direct catalytic effect on the allyl chloride addition itself.

In all cases, the product isolated was the "normal" addition product, 1-chloro-2-iodopropane.

The Addition of Hydrogen Iodide to 1-Bromopropene

The addition of hydrogen iodide to 1-bromopropene has not been recorded previously. Kharasch, Engelmann, and Mayo¹ reported that the "normal" addition of hydrogen bromide and the addition of hydrogen chloride in the presence of ferric chloride gave a mixture consisting of about one-third of the 1,1-dihalide and two-thirds of the 1,2-dihalide. With hydrogen bromide, the addition was extremely susceptible to the effects of peroxides, for the best experiments with antioxidants yielded only 8 per cent of the 1,1-dihalide in the addition product. It seemed, therefore, that 1-bromopropene would serve as an excellent test of whether hydrogen iodide had any tendency whatever to give an "abnormal" addition, as well as to provide a test of the composition of the "normal" addition product. The product obtained by addition of hydrogen iodide to a mixture of the cis- and trans- isomers was a mixture of about one-third of the 1,1-dihalide and two-thirds of the 1,2-dihalide and the proportion was not influenced by the presence or absence of peroxides or iodine.

The addition was comparatively slow, requiring about two days at 0°. Iodine appeared to have little or no catalytic effect, and this is interpreted as indicating the extreme instability of the iodine addition product of 1-bromopropene. The low-boiling portion of the reaction product was shown by its boiling range to be mostly unchanged 1-bromopropene and therefore little or no reduction had taken place. Where larger quantities of reactants were used to decrease the experimental error of the analyses, there was found 36 per cent of the 1,1-dihalide in the addition product. The 21 and 24 per cent of 1,1-dihalide reported in the other two experiments are thought not to be significant because of the small quantities of addition products obtained.

¹Kharasch, Engelmann, and Mayo, J. Org. Chem., 2, 288 (1937).

TABLE 7
THE ADDITION OF HYDROGEN IODIDE TO 1-BROMOPROPENE^a

Expt. No.	Moles ^c HI	Added Substances	Moles ^c	Reaction		Yield		Proportion ^b 1,1-dihalide in Mixture %
				Time (Hr.)	Temp. (°C.)	Addition ^c Product	Low-boiling Fraction	
95	1.12	I ₂	0.014	12	0	74	18	24
99	1.16	None	-----	27	0	87	12	21
111	1.18	None	-----	45	0	76	20	36

^{a, c, d} Have the same significance as in Table 5. 10 gm. of peroxide-free 1-bromopropene used in first two experiments, and 17.6 gm. of 1-bromopropene containing peroxide in the last experiment.

^b The remainder of the product was 1-bromo-2-iodopropane.

Discussion

The proportions of 1,1-dihalide obtained in the addition of hydrogen iodide to 1-bromopropene (36 per cent) is in striking agreement with the proportions found in the addition of hydrogen bromide (33, 33, and 41 per cent) and hydrogen chloride (35 and 36 per cent) in the presence of ferric chloride.^{1,2} Similarly, the addition of hydrogen iodide corresponds to the "normal" addition of hydrogen bromide and the addition of hydrogen chloride to propene, vinyl chloride, allyl chloride, allyl bromide, 1-butene, neopentylethylene, and vinyl bromide, although but one halide is formed in each of these cases. Since direction of addition of hydrogen iodide is not complicated by a "peroxide effect," this addition may be taken as a standard for the "normal" addition of a halogen acid, just as the addition of hydrogen chloride in the presence or absence of ferric chloride or the addition of hydrogen bromide in the presence of ferric chloride has been shown³ to serve as a standard for the "normal" addition.

Experimental Part

Materials and reagents.--Propene and propane of higher than 99 per cent purity were obtained from commercial sources. The pentane used was a commercial pentane-isopentane mixture. Allyl bromide⁴ and allyl chloride⁵ were prepared from allyl alcohol, concentrated hydrochloric acid or anhydrous hydrogen bromide and 1-2 per cent of the corresponding cuprous halide. 1-Bromopropene was prepared by treatment of propene dibromide with alcoholic sodium ethylate.⁶ Washing the crude product with dilute sulfuric acid was found essential to remove unsaturated ethers which were otherwise insepa-

¹Kharasch, Engelmann, and Mayo, J. Org. Chem., 2, 288 (1937).

²Kharasch, Kleiger, and Mayo, J. Org. Chem., 4, 428 (1939).

³Ibid.

⁴Kharasch and Mayo, J. Am. Chem. Soc., 55, 2468 (1933).

⁵Dewael, Bull. soc. chim. Belg., 39, 40 (1930).

⁶Kharasch, Engelmann, and Mayo, J. Org. Chem., 2, 288 (1937).

rable by fractionation.

Hydrogen iodide was prepared by the very convenient method of Houben, Boedler, and Fisher¹ by refluxing a mixture of tetralin and iodine. Yields of better than 96 per cent of crude hydrogen iodide (containing 2-3 per cent of tetralin) were consistently obtained by this method. The gas was collected in a large trap containing some phosphorus pentoxide and a mercury mirror (prepared by heating a drop of mercury in the trap before addition of phosphorus pentoxide). The trap was cooled in dry ice-acetone. After collection, the gas was distilled in the absence of air into the storage vessel which was a large 30 mm. glass tube containing a mercury mirror and equipped with ground joint and stopcock. The usual high-vacuum technique² was employed for this purpose. Air was not permitted to come in contact with the hydrogen iodide, which therefore remained colorless. The storage vessel was kept in dry ice-acetone when not in use.

Experimental procedure.--In all experiments up to and including number 125, the following procedure and all-glass apparatus were used: Four or five vertical tubes were attached to a horizontal tube which was connected to a mercury diffusion pump via a stopcock. The mercury pump was capable of producing a vacuum of 10^{-5} mm. of mercury pressure. Transfer of materials from one tube to the other was effected by distillation in high vacuum with appropriate manipulation of stopcocks and cooling baths (usually liquid nitrogen). Traces of noncondensable gases were removed after each operation by re-evacuation of the system.

The first two vertical tubes were attached to the system so that they were separated from the mercury pump by one stopcock and from the other two or three tubes by another stopcock. The first tube ended in a ground joint so that the hydrogen iodide storage vessel could be attached to it. The second tube served only for rough estimation of the hydrogen iodide withdrawn from the storage tube. Better estimation (to ± 0.3 g.) of this quantity was made at the conclusion of an experiment when the final weight of the cold hydrogen iodide storage vessel was compared with its initial weight.

¹Houben, Boedler, and Fisher, Ber., 69B, 1773 (1936).

²Kharasch and Mayo, J. Am. Chem. Soc., 55, 2468 (1933).

The third vertical tube, separated from the mercury pump by both stopcocks, was the one in which the addition reaction was carried out eventually. At the beginning of an experiment it contained only water and/or such components of the reaction mixture as were not readily volatile at room temperature: iodine, diphenylamine, ascaridole, etc. The fourth tube contained the ethylene derivative and often the solvent and a little phosphorus pentoxide. When the solvent was acetic acid or nitrobenzene, a fifth tube was employed so that the propene and solvent could be dried and degassed separately. Materials in the third, fourth, and fifth tubes were weighed out in these tubes to ± 0.1 g. before the tubes were attached to the assembly. All materials not already in the reaction tube were finally distilled into that tube which was then (except as noted in the tables) sealed off without entrance of air.

In all experiments above number 125, hydrogen iodide and propene were measured gasometrically in a bulb equipped with a manometer. The gases from the measuring bulb were condensed before distilling into the bomb tubes; this procedure removed small amounts of noncondensable gases, mercury, and mercuric iodide, which were present mostly in the hydrogen iodide. High boiling materials were placed in the bomb tube directly, as before. Allyl chloride was stored in a container permanently attached to the vacuum line and was estimated by liquid volume in a calibrated bulb. Low boiling materials and solvents were placed in a separate tube attached above the reaction tube, from which tube they were distilled directly into the reaction tube. Use of phosphorus pentoxide in the solvent was a part of the regular procedure.

Allyl chloride and allyl bromide received a preliminary treatment before being placed in the system. This consisted of agitation with acidulated ferrous sulfate solution to destroy peroxides, after which the materials were rapidly dried over phosphorus pentoxide and distilled.

Iodine used in allyl chloride experiments was weighed in sealed capsules to the tenth of a milligram. These were broken and placed in the bomb tube just before the latter was attached to the assembly. Appropriate refrigeration was employed on evacuation. In other cases, iodine was weighed on the rough balance.

Reactions at 0° were carried out in an ice water mixture. In experiments with allyl chloride, it was found that less iodine

was produced when the bomb tube was totally immersed in the liquid bath than if only the liquid phase were cooled.

The course of the addition could be followed by observation of the liquid level because the volume of the reaction mixture decreased about ten per cent during the reaction, depending on the olefin used. The bomb tube was held vertically, and the height of the meniscus from the bottom measured with a metric rule. After the desired length of time, the bomb tubes were cooled in dry ice-acetone and the tops cut off. Several procedures were used for the analysis of the reaction products: (1) The bomb contents were washed with aqueous sodium sulfite and potassium carbonate to remove iodine and hydrogen iodide, dried over anhydrous potassium carbonate and distilled through a Podbielniak¹ column. A single fraction of boiling-point corresponding to the "normal" addition product was obtained. In propene experiments the yield was determined from the weight of washed but undried product; in other cases, from the weight of the addition product after fractionation. Procedure (2) differed in that the distillate was cut into several fractions and the index of refraction of each was determined. In procedure (3) the bomb contents were distilled at about 10 mm. pressure of mercury into a trap cooled by dry ice-acetone and the weight of the distillate thus collected was taken as the weight of addition product formed. Thereafter, the product was treated as in procedure (2). In procedure (4) the washing process was replaced by titration of the iodine present with standard sodium thiosulfate, back-titrating with standard iodine if necessary. Thereafter, the procedure was as in (2).

All propene experiments up to and including number 125 were analyzed according to procedure (1). The distillates of all experiments analyzed by this method were combined and refractionated. The index of refraction of the main fraction corresponding with the value for isopropyl iodide. The fore-runs and residues had lower indices, excluding the possibility that the residues might contain n-propyl iodide. This was also generally true of the various fractions of experiments 126-134, analyzed by procedure (2). Those above number 134 were analyzed according to procedure (3); but none gave any indication of the formation of n-propyl iodide. The preliminary vacuum distillation in (3) was

¹Podbielniak, Ind. Eng. Chem., Anal. Ed., 5, 119 (1933).

a distinct improvement in technique, since it removed traces of unreacted propene and thus caused the indices of refraction of the fore-runs of the fractionations to correspond more closely with the index of refraction of isopropyl iodide.

In certain instances experiments had been carried out in which n-propyl iodide was added to the reaction mixture of propene and hydrogen iodide. Such reaction mixtures were analyzed according to procedure (3). The composition of the fractions was ascertained by index of refraction, it having been found that the index of refraction of a mixture of n- and isopropyl iodides is a linear function of the composition.

Ingold and Ramsden did not describe their procedure fully. In attempts to reproduce their results, the following procedure was employed: Propene was condensed in a small bomb tube in the absence of air, using high-vacuum technique. The end of this tube was drawn out to a long capillary, and the tube was slipped into a larger bomb tube after being sealed while cold. The open end of the large bomb tube was drawn down (meanwhile the other end, containing the propene bomb tube, was occasionally cooled in liquid nitrogen) and was sealed onto the vacuum line. Then, after evacuation, hydrogen iodide (and solvent, if any) were distilled into the large bomb tube and the whole was sealed from the line. The bomb was allowed to warm to room temperature and by suitable manipulation the long capillary was shattered and the contents mixed. After reaction, the products were analyzed according to procedures (1), (2), or (3) as indicated above.

Allyl bromide experiments were conducted according to procedure (2), using a pressure of 20 mm. for the fractionation. Residues were contaminated with too much tar, iodine, and carbonaceous material to allow further analysis. Low-boiling materials were collected in a trap cooled by dry ice-acetone or liquid nitrogen. Reaction mixtures containing ascaridole residues yielded hydrogen bromide in the low-boiling fraction unless a preliminary distillation of the product was conducted at a pressure of less than 0.1 mm. of mercury. The yields of addition product were rather low in such cases. A preliminary vacuum distillation of the product at less than 0.1 mm. pressure as described removed the ascaridole residues and high yields of addition product, smaller amounts of low-boiling material, and no hydrogen bromide were obtained.

Allyl chloride experiments were conducted according to (4) when determinations of free iodine were made. Otherwise they were conducted according to (2). The fractionations were conducted at 40 mm. pressure of mercury.

Reduction products of allyl bromide.--The low-boiling materials from a number of allyl bromide experiments were combined and fractionated through the Podbielniak column. They consisted of about 40 per cent allyl bromide and a like amount of isopropyl iodide, and also 10 per cent of isopropyl bromide. The last was identified by halogen analysis and preparation of isopropyl 3,5-dinitrobenzoate.

1-Bromo-1-iodopropane.--The various fractions from the 1-bromopropene experiments were combined and fractionated in order to obtain a sample of 1-bromo-1-iodopropane. The amount of available material was too small to permit isolation of a pure sample, and an estimate of the index of refraction had to be made. Fractions having indices both above and below this estimated value were obtained, and it is believed that the error in this index of refraction is less than 0.0010.

Structure of 1-chloro-2-iodopropane.--The structure of the addition product of hydrogen iodide and allyl chloride was partially proved by the action of zinc and hot alcohol on the addition product. An 87 per cent yield of propene was obtained, and this was identified by its addition of hydrogen iodide to give a nearly theoretical yield of isopropyl iodide. Had the product been a 1,3-dihalide, the product would have been cyclo-propane. This yields n-propyl iodide with hydrogen iodide. A 1,1-dihalide would have given hexene-3, and thus it is proved that the halogens are in the 1,2-position.

It was then shown that the 1,2-dihalide was 1-chloro-2-iodopropane by adding it to an equimolar proportion of sodium ethoxide dissolved in warm alcohol. The product was a mixture of the cis- and trans-isomers of 1-chloropropene, identified by boiling-point and index of refraction. If the ethoxide solution were added to the addition product, the main reaction product was propene, for the sodium iodide first formed underwent a Finkelstein¹

¹Finkelstein, Ber., 43B, 1528 (1910).

reaction with the remaining 1-chloro-2-iodopropane to give propene diiodide which decomposed into propene and iodine at the temperature used. The iodine appeared in the reaction product as iodoform, due to the alkali present. The Finkelstein reaction was minimized by keeping the alkali always in excess of the addition product. A complex-ion former such as mercuric chloride or oxide should further minimize the Finkelstein reaction.

Summary

Thorough investigation of the addition of hydrogen iodide to propene, allyl bromide, and allyl chloride has shown that only one addition product can be obtained in each case. The addition of hydrogen iodide to 1-bromopropene yields a mixture of one-third 1,1- and two-thirds 1,2-dihalides. In all the above cases the products obtained correspond to those obtained in the additions of hydrogen chloride and the "normal" additions of hydrogen bromide. It is shown that iodine is a powerful catalyst for the addition of hydrogen iodide and that experimental conditions may influence the rate of addition through their effect on the rate at which iodine is brought into solution. Mercuric iodide was shown to be a catalyst for the propene- hydrogen iodide addition.

1-Chloro-2-iodopropane was prepared pure for the first time and its structure elucidated completely.

1-Bromo-1-iodopropane was formed but not isolated in the pure state.

TABLE 8

PHYSICAL CONSTANTS OF HALOHYDROCARBONS

Compound	Boiling Point		Index of Refraction (n_D^{20})
	(760 mm.)	(20 mm.)	
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{I}^a$	102.4° (102.2°) ^a	----	1.5052 (1.5051) ^g (1.50508) ^c
$\text{CH}_3\text{-CHI-CH}_3$	89.6° (89.5°) ^a	----	1.4988 (1.4985) ^g (1.49969) ^c
$\text{CH}_3\text{-CHI-CH}_2\text{Br}$	Decomposes	66.8° (66.2°) ^g	1.5916 (1.5914) ^g
$\text{CH}_3\text{-CH}_2\text{-CHIBr}$	Decomposes	61.3° (estd.)	1.5826 (estimated)
$\text{CH}_3\text{-CHI-CH}_2\text{Cl}$	147° (sl. dec.) ^e	66.2° (50 mm.)	1.5472
$\text{CH}_2\text{I-CH}_2\text{-CH}_2\text{Cl}$	(170-172°) ^d	----	----
$\text{CH}_3\text{-CHCl-CH}_2\text{I}$	(147°)	----	----
$\text{CH}_2\text{=CH-CH}_2\text{Br}$	69.5° (69.6°) ^f	----	1.4688 (1.4693) ^f
$\text{CH}_2\text{=CH-CH}_2\text{Cl}$	44.6°	----	1.4151
cis- $\text{CH}_3\text{-CH=CHBr}$	58.8° (58.7°) ^b	----	----
trans- $\text{CH}_3\text{-CH=CHBr}$	64.2° (750 mm.)	----	1.4530

^aLinneman, Ann., 159, 25 (1872).^bKharasch, Engelmann, and Mayo, J. Org. Chem., 2, 288 (1937).^cInternational Critical Tables, " McGraw-Hill Book Co., Inc., New York, 1920, 7, 35.^dHenry, Bull. soc. chim. Paris, (3) 17, 93 (1897).^eSorokin, Zelt. Chem. (1870) 519.^fKharasch and Mayo, J. Am. Chem. Soc., 55, 2468 (1933).^gKharasch and Hannum, J. Am. Chem. Soc., 56, 1762 (1934).

CHAPTER III

SOME DERIVATIVES OF HIGHER BENZENE HOMOLOGUES

Introduction and Previous Work

The investigation of certain of the derivatives of the higher benzene homologues was undertaken with the objects of (a) development of methods of synthesis and (b) study of the effects of the introduction of large groups into the molecules of the simple benzene derivatives. The effects of such groups may be interpreted in several ways, the most important of which are steric hindrance effects arising from group size and position, and phenomena resulting from a change in the electronegativity of the phenyl group upon substitution in the nucleus. For examples of these phenomena, let one consider the case of 2,4,6-triisopropylaniline. It was of interest to discover if the size of the isopropyl groups in the 2 and 6 positions were such as to hinder or prevent diazotization and coupling reactions. The greater electronegativity of the 2,4,6-triisopropylphenyl group as compared with the phenyl group could be qualitatively followed by comparing the basicity of the substituted aniline with aniline itself.

Most of the present work was conducted with 1,3,5-triisopropylbenzene and its derivatives. Some work was done in the direction of 1,3,5-tri-tertiarybutylbenzene and its derivatives; but inasmuch as the synthesis of the latter hydrocarbon presented many complications which were absent in the synthesis of the former, it was felt that the problem could be best attacked by the initial elucidation of methods of synthesis and determination of the properties of s-triisopropylbenzene and its derivatives. In this way it was felt that methods of attack on the problem of the quantity preparation of s-tri-tertiarybutylbenzene would suggest themselves. As it later developed, time did not permit successful exploitation of the problem of preparation of s-tri-tertiarybutylbenzene. Therefore the only discussion of the compound in this paper will be a description of attempts to prepare the hydrocarbon.

Syntheses of polyalkylated benzenes.---Methods which were given in

the literature included the Wurtz-Fittig¹ reaction between 1,3,5-tribromobenzene, sodium, and an alkyl halide in an ether medium; the distillation of methyl ketones with a dehydrating agent; and various modifications of the Friedel-Crafts type of condensation.

The yields of symmetrically substituted benzenes obtained by distillation of aliphatic methyl ketones with a dehydrating agent decrease rapidly as the series is ascended.² Thus, methyl ethyl ketone gave but a three per cent yield of *s*-triethylbenzene when distilled with sulfuric acid. Similarly methyl *n*-propyl ketone gave scarcely any *s*-tri-*n*-propylbenzene, even when a variety of dehydrating agents was used.

Among the various modifications of the Friedel-Crafts type of condensation which have been used in the direct polyalkylation of benzene are the following: Use of boron trifluoride or sulfuric acid or a combination of the two with an olefin;^{3,4} phosphoric acid and an olefin,⁵ sulfuric acid and a carbinol;^{6,7} aluminum chloride and an olefin;^{8,9,10,11} and aluminum chloride and an alkyl halide.¹² The general conclusions that have been drawn are that either sulfuric acid, or boron trifluoride, or a mixture of the

¹Fittig, Ann., 139, 178 (1866).

²Jacobsen, Ber., 7, 1435 (1874); ibid., 8, 1259-61 (1875).

³Croxall, Sowa, and Nieuwland, J. Am. Chem. Soc., 57, 1549 (1935).

⁴Ipatieff and von Grosse, J. Am. Chem. Soc., 58, 2339 (1936).

⁵Ipatieff, Pines, and Komarewsky, Ind. Eng. Chem., 28, 222 (1936).

⁶Meyer and Berhauer, Monats., 53-4, 721-52 (1929).

⁷Kirrmann and Graves, Bull. soc. chim. France, (5) 1, 1494 (1934).

⁸Berry and Reid, J. Am. Chem. Soc., 49, 3142 (1927).

⁹Gatterman, Fritz, and Beck, Ber., 32B, 1122 (1899).

¹⁰Balsohn and Friedel, Bull. soc. chim. Paris, (2) 33, 340 (1880).

¹¹Balsohn and Friedel, Bull. soc. chim. Paris, (2) 34, 635 (1880).

¹²Gustavson, J. prakt. Chem., (2) 72, 57 (1905).

two will promote ortho-para alkylation, while phosphoric acid or aluminum chloride will promote meta-alkylation. Olefins do not prove as satisfactory as alkyl halides in the synthesis of tri-alkylated benzenes, for the halides result in the production of a purer product. Normal propyl alcohol with aluminum chloride and benzene gave n-propylbenzene instead of the expected cumene.

On the basis of these reports, the method chosen for the synthesis of 1,3,5-trisopropylbenzene was that of Gustavson.^{1,2} It was pointed out by him that it was important to use one mole of aluminum chloride (calculated as AlCl_3) per mole of benzene in order to obtain best results. It was also highly desirable to have the aluminum chloride finely ground. In this work aluminum chloride was used which would pass a 60-mesh sieve.

Discussion of Results

Excellent yields of s-trisopropylbenzene were obtained by Gustavson's method, the yield with large preparations being well over 90 per cent. The method was not nearly as successful when applied to the preparation of tri-tertiarybutylbenzene, a mixture of substances being obtained.

Trisopropylbenzene nitrates with about the same ease as does mesitylene. Indeed, for the preparation of nitrotrisopropylbenzene, the same conditions must be used that are ordinarily employed in the preparation of nitromesitylene. Nitric-sulfuric acid mixture produces dinitrotrisopropylbenzene, but apparently the trinitro-compound cannot be prepared. This is assumed to be due to steric hindrance factors. The first two nitro groups to enter are assumed to bend two isopropyl groups over the unoccupied position on the nucleus, thus protecting it from attack and substitution. The dinitro-compound responds faintly to the Janovsky test.³

On standing in diffuse sunlight for a period of a few days, nitrotrisopropylbenzene acquired a brick-red surface discoloration while dinitrotrisopropylbenzene turned brown on the surface. These phenomena recall similar phenomena observed by Steiger⁴

¹Ibid.

²Gustavson, Compt. Rend., 140, 940 (1905).

³Janovsky, Ber. 24, 971 (1891).

⁴Steiger, Helv. 16, 793 (1933); ibid., 17, 701, 1359 (1934).

with perimethylnitronaphthalene and 8-nitro-alpha-naphthyl benzyl sulfone. These may be explained on the basis of interference of nitro- and methyl groups, light supplying the necessary energy of activation for an intramolecular reduction and oxidation. The colors are thus due to nitroso-, azo-, azoxy-, and hydroxylamino-compounds formed by the reaction.

In contrast with nitrobenzene and ortho-nitrotoluene, alcoholic stannous chloride reduced nitrotriisopropylbenzene very sluggishly, refluxing for twelve hours being necessary for a reduction to 2,4,6-triisopropylaniline. Zinc and acetic acid accomplished the reduction with much greater facility. When such a reaction mixture was diluted with several volumes of water, the amine separated and could be extracted with ether without the necessity of neutralizing the acetic acid. Reduction of dinitrotriisopropylbenzene with zinc and acetic acids gave the diamine which could be extracted from diluted acetic acid solution, but with greater difficulty than triisopropylaniline because of the greater basicity of the diamine. Both amines formed hydrochlorides which were sparingly soluble in water, but soluble in alcohol and highly soluble in ether. For this reason the amines cannot be extracted from their ether solutions by hydrochloric acid.

Nitrotriisopropylbenzene could not be reduced catalytically with Adams' catalyst¹ and hydrogen. Four attempts were made, and the recovered catalyst was sufficiently active to destroy the filter paper in a few minutes.

Both 2,4,6-triisopropylaniline and 2,4,6-triisopropyl-m-phenylenediamine were found to be diazotizable. The coupling products with beta-naphthol were brilliant orange products, sparingly soluble in alkali.

2,4,6-Triisopropylaniline hydrochloride forms white needles which are extensively hydrolyzed by water. On exposure to air, hydrogen chloride is lost to such an extent that under suitable conditions its odor can be detected. A saturated aqueous solution of the hydrochloride precipitates the salt on addition of concentrated hydrochloric acid. The corresponding sulfate is nearly insoluble in water. Neutral equivalent determinations conducted on either salt give high results, due to loss of acid on

¹Adams et al., J. Am. Chem. Soc., 45, 2171 (1923); ibid., 49, 1093 (1927).

TABLE 9

PHYSICAL CONSTANTS OF TRIISOPROPYLBENZENE DERIVATIVES

Compound	Melting Point	Boiling Point	n_D^{20}	Nitrogen, Calculated (%)	Nitrogen, Found (%)
1,3,5-triisopropylbenzene	Below -80°	229-231°	1.4891	---	---
2,4,6-triisopropyl nitrobenzene	72- $\frac{1}{2}$ °	-----	-----	5.67	5.79; 5.69
1,3-dinitro-2,4,6-tri- isopropylbenzene	135- $\frac{1}{2}$ °	-----	-----	9.59	9.62; 9.83
2,4,6-triisopropyl proylaniline	Forms Glass	259-263°	-----	6.39	-----
1,3-diamino-2,4,6-tri- isopropylbenzene	Forms Glass	295-300°	-----	11.97	-----
2,4,6-triisopropyl acetanilide	175- $\frac{1}{2}$ °	-----	-----	5.36	5.58; 5.49
1,3-diacetamino-2,4,6- triisopropylbenzene	Above 360°	-----	-----	8.81	8.85; 8.80

standing.

By treatment with acetic anhydride and pyridine, 2,4,6-triisopropylaniline formed sym-triisopropylacetanilide, white crystals soluble in alcohol. Nitrogen analyses agreed well with calculated values. In a similar fashion, 2,4,6-triisopropyl-m-phenylenediamine gave 1,3,5-triisopropyl-2,4-diacetaminobenzene. This substance was insoluble in all of the following solvents: Methyl and ethyl alcohols, acetic acid, acetone, chloroform, heptane, benzene, and even triisopropylbenzene. It was found to be very slightly soluble in boiling triisopropylbenzene for on cooling the solution, a few needles separated. Its solubility in boiling triisopropylbenzene is estimated at 1 mg. per 10 cc. of solvent. The product was therefore purified by extraction with several solvents, and nitrogen analyses agreed excellently with theory. Its melting point was not determined but is above 360°.

Experimental Part

Materials and reagents.--Isopropyl chloride was prepared from the corresponding alcohol by the method of "Organic Syntheses."¹ The purified product had a boiling range of 35.5-.8°.

Aluminum chloride was a commercial product of the highest quality; it was ground to pass a 60-mesh sieve. Benzene was a commercial thiophene-free product.

Preparation of 1,3,5-triisopropylbenzene.--Small scouting experiments were conducted using 0.3 mole each of benzene and aluminum chloride (calculated as AlCl_3), and 0.9 mole of isopropyl chloride. When success of the technique of preparation was assured, larger-scale preparations were made. Details of the largest-scale experiment follow:

Four moles (535 g.) of anhydrous aluminum chloride were placed in a five-liter three-necked flask equipped with a heavy-duty high-speed centrifugal stirrer, mercury seal, reflux condenser, dropping funnel, and hydrogen chloride absorption apparatus. Four moles of benzene were added via the dropping funnel, and the whole thoroughly mixed and cooled to +5°. Four moles of isopropyl chloride were added slowly through the dropping funnel.

¹"Organic Syntheses," John Wiley and Sons, New York City, 1925, 5, 28.

The temperature was then lowered to -10° , and eight moles of isopropyl chloride added slowly. A yellow crystalline material began to separate when the addition of the last four moles had begun, and this comprised most of the material in the flask when all the chloride had been added. The stirrer, mercury seal, dropping funnel, and condenser were removed and the contents thoroughly mixed by hand until the material was a pure yellow, and was free of green streaks and splotches. The product was now a dry, crystalline, yellow powder, of empirical formula¹ $\text{Al}_2\text{Cl}_6(\text{C}_6\text{H}_3(\text{C}_3\text{H}_7)_3)_2 \text{HCl}$. This was decomposed by ice and hydrochloric acid and the upper layer separated from the aqueous layer and small amounts of insoluble materials, washed with water and dried over potassium carbonate. The aqueous layer and insolubles were extracted with ether. The extract was washed with water and dried separately over potassium carbonate. By means of several distillations, the main fraction and ether extract gave a 93 per cent yield of material boiling at $229-231^{\circ}$. Fractionation of a sample of this material into eight fractions in a small distilling apparatus gave three fractions of identical index of refraction, which value was taken as that of 1,3,5-triisopropylbenzene.

Attempted preparation of 1,3,5-tri-tertiary butylbenzene.--

Gustavson² reported the formation of a yellow complex when tertiary butyl chloride was substituted for isopropyl chloride in the above preparation. Scouting runs were employed in this phase of the work. The size of my preparations did not pass the scouting stage. When experiments were conducted exactly as with isopropyl chloride except for the substitution of tertiary butyl chloride, the final reaction product was not dry and powdery, but a dirty-yellow, thick mud. On decomposition with ice and hydrochloric acid, the product was obtained as a slate-colored liquid. When this was distilled, materials boiling from the boiling point of ether (which was used to extract the product from the aqueous layer) to above 400° were obtained, without the appearance of any well-defined fractions. It was found that if the last one-third of the tertiary butyl chloride were mixed with one- or two-thirds its volume of ether before being added to the reaction mixture, the product gave a fairly well-defined fraction boiling between

¹Gustavson, J. prakt. Chem., (2) 72, 57 (1905).

²Ibid.

240° and 280°. If the ether had been added to the benzene-aluminum chloride mixture before any tertiary butyl chloride had been added, the fractions were still further defined, for about two-thirds of the product boiled between 235° and 245°. Substitution of carbon bisulfide for ether also facilitated formation of a 235-245° product, but the results were not as clear-cut as with ether. Ligroin was of no aid whatever.

These 235-245° fractions partially crystallized on standing, and by repeated crystallization from methyl alcohol or methyl alcohol-water at -78° resulted in the isolation of a crystalline product which had a true (not capillary) melting-range of 46-52°. It was provisionally assumed to be *s*-tri-tertiarybutylbenzene. The yield of this material was but 40 per cent. Molecular weight determinations gave decidedly low values.

Friedel-Crafts reaction with phthalanil.--A Friedel-Crafts reaction was attempted using 0.1 mole each of phthalanil and aluminum chloride with 0.3 mole of tertiary butyl chloride and 50 cc. of carbon bisulfide as solvent. Some hydrogen chloride was evolved, but the sole amine found after hydrolysis of the reaction product with alcoholic potash was aniline.

Nitration of 1,3,5-triisopropylbenzene.--Attempts to produce 2,4,6-triisopropyl nitrobenzene by nitration of the hydrocarbon with nitric-sulfuric acids resulted in meager success at best. By reduction of the amount of nitric acid to the theoretical quantity necessary for the nitration, the yield of 2,4,6-triisopropyl nitrobenzene could be raised to 20 per cent; but there was also formed about 10 per cent of 1,3,5-triisopropyl-2,4-dinitrobenzene, and a large proportion of the hydrocarbon remained unattacked. The volume of the sulfuric acid had to be at least ten times that of the nitric acid, or else the dinitro-compound was formed at the expense of the mono-nitro compound. If a nitrating mixture composed of one-half volume of concentrated nitric acid, the same volume of sulfuric acid, and two volumes of acetic acid, the proportion of mono-nitro compound was greatly raised; but the best results were obtained by employing an adaptation of the method of "Organic Syntheses"¹ for the preparation of nitromesitylene by nitration of

¹"Organic Syntheses," John Wiley and Sons, New York, 1934, 14, 68.

mesitylene. The sole change made was the substitution of the same number of moles of 1,3,5-triisopropylbenzene for the quantity of mesitylene required in the nitromesitylene preparation. With this method, a yield of 87 per cent of the mononitro-compounds could be obtained in the final distillation. On crystallization from methyl alcohol white needles were obtained which reddened on the surface when exposed to light for a few hours. The crystals melted to a light yellow liquid, which remained yellow in the massive condition.

1,3,5-Triisopropyl-2,4-dinitrobenzene can be prepared by nitration of the mononitro-compound with nitric-sulfuric acids mixture, but it was usually prepared by nitration of the hydrocarbon with these acids. The best, cleanest material was obtained when a mixture of equal volumes of the hydrocarbon and carbon bisulfide was whipped with three to four volumes of nitric-sulfuric acids mixture (equal volumes of the two acids) at about 0°; after a half-hour the temperature may be raised until the carbon bisulfide has been driven off. If conducted without a solvent, larger amounts of hydrocarbon are left unattacked than in the presence of a solvent. If conducted at a higher temperature, the nitration proceeds more rapidly; but the product is contaminated with brown tarry materials as well as nitrogen oxides. The stirring is essential to the smooth progress of the reaction.

After most of the carbon bisulfide was driven off, the acid layer was decanted from the semi-solid material. This material was then washed with water, and a few cubic centimeters of methyl alcohol added and the product washed onto the suction filter. It was recrystallized from methyl alcohol or methyl alcohol-water. The leaflets were white when pure, but darkened on exposure to light for several hours.

Attempts to prepare the corresponding trinitro-compound by nitration of the dinitro-compound with fuming nitric and concentrated sulfuric acids resulted in failure. Products were obtained which contained less nitrogen than the starting material.

Reduction of 2,4,6-triisopropyl nitrobenzene.---An alcoholic solution of stannous chloride reduces the mononitro-compound sluggishly. Refluxing for twelve hours was usually necessary. The same reagent reduced ortho-nitrotoluene vigorously. The product (2,4,6-triisopropyl aniline) was recovered from the reaction

mixture by distilling off the alcohol, adding small amounts of hydrochloric acid from time to time to prevent the base from distilling with the alcohol. The residue was diluted with water, and rendered strongly alkaline with sodium hydroxide. After cooling, the solution was extracted with ether which was subsequently dried over potassium carbonate and distilled. The amine was isolated as a brown oil which did not crystallize at -80° , either alone or dissolved in a small amount of methyl alcohol. The yield by this method was in the vicinity of 50 per cent.

Zinc and acetic acid performed the reduction much more rapidly. The nitro-compound was dissolved in twenty times its weight of glacial acetic acid warmed to 60° , and zinc dust added cautiously until twice the theoretical amount had been added. The mixture was refluxed in a flask of three to four times the volume of the mixture, since it was prone to froth. After half an hour, the mixture was poured into five times its volume of ice water. The amine formed a layer on the surface of the liquid; and, after saturating with salt, the amine was extracted with ether. Evaporation of the solvent gave the amine as a dark red oil which was not as pure as that obtained by stannous chloride reduction. The yield was 80 per cent after distillation.

Reduction of 1,3,5-triisopropyl-2,4-dinitrobenzene.---A stannous chloride reduction was carried out with this compound in essentially the same way described for the mononitro-compound. However, no diamine was isolated, because the ether extract of the solution obtained after evaporation of the alcohol and alkalizing with sodium hydroxide was itself extracted with hydrochloric acid. The intention was to free the amine of any unreduced nitro-compound and it was assumed that the amine would pass into the aqueous phase as the hydrochloride. Since the hydrochloride is much more soluble in ether than in water, no amine was found on working up the hydrochloric acid layer of this extraction. Earlier, however, a sample of the alcoholic solution had been treated with sodium nitrite and acid, and beta-naphthol was added. The development of an intense color indicated that the amine had been formed and that it was diazotizable.

Zinc and acetic acid were also used as reducing agent. The procedure employed parallels that used for the similar reduction of the mononitro-compound, except that on dilution of the

acetic acid, the diamine did not separate from solution. Therefore six ether extractions were necessary in order to avoid the necessity of neutralizing the acetic acid. On distillation of the ether extract, the diamine was obtained as a brownish-yellow strongly fluorescent oil which became very viscous when cool. With or without solvent, it did not crystallize at -80° . The yield after distillation was 64 per cent.

Preparation of 2,4,6-triisopropylacetanilide and 1,3,5-triisopropyl-2,4-diacetaminobenzene.---The appropriate amine was treated with a mixture of acetic anhydride and pyridine. If the diamine had been employed, the solution soon set to a thick paste. The product was either insoluble or else very sparingly soluble in all the common solvents, and had a very low solubility in the parent hydrocarbon. It was possible to isolate a few needles from solution in triisopropylbenzene. For nitrogen analysis, it was purified by extracting successively with alcohol, acetic acid, chloroform, and acetone. Its melting-point was not determined, but is above 360° .

If triisopropylaniline were being acetylated, the mixture of the amine with acetic anhydride and pyridine was warmed on the steam bath for a few minutes and then poured into cold water, and the product recrystallized from methyl alcohol. Difficulties were encountered if the crude amine prepared by the zinc-acetic acid reduction were used, since a bright red impurity was formed. The greater part of the impurity could be removed by preparation of the amine hydrochloride and recrystallizing this from a concentrated alcoholic solution by addition of concentrated hydrochloric acid. The hydrochloride was then added to the acetylating mixture. The product was precipitated as usual, and recrystallized from aqueous formic or acetic acid. In general, the impurity could be made to form a globulus which could be removed from the solution. After recovery from this solution, the product was recrystallized from methyl alcohol or methyl alcohol-water. The solutions tended to supersaturate very easily and oftentimes seeding had to be resorted to. The substituted anilid crystallized in pure white needles from alcohol.

Structure of 1,3,5-triisopropylbenzene.---Gustavson¹ claimed to

¹Gustavson, J. prakt. Chem., 72, 57 (1905).

have proved the structure of 1,3,5-triisopropylbenzene obtained by him when he obtained a small amount of trimesic acid, by nitric acid oxidation of the hydrocarbon. It was found in the present work that no oxidation of the hydrocarbon occurred when it was refluxed for a week with a concentrated solution of chromic anhydride in 6-normal sulfuric acid. Neutral potassium permanganate had no effect.

An attempt was made to prove the structure by chlorinating the hydrocarbon to 1,3,5-tri-(2-chloroisopropyl-)benzene by use of sulfuryl chloride and benzoyl peroxide.¹ The reaction product with a slight excess of sulfuryl chloride was oxidized with the calculated quantity of potassium permanganate. The filtered solution was acidified and extracted with ether. Crystals were obtained in a quantity barely sufficient for a melting point. These melted at 80-83°, which is far below the melting-point of trimesic acid.

Despite the fact that aqueous chromic acid does not attack the hydrocarbon, the material was rapidly oxidized when acetic acid was used as solvent. The product was rather inconvenient to work up, since oxidation of one mole of triisopropylbenzene to trimesic acid requires 18 moles of chromic anhydride. After oxidation was complete, the acetic acid was distilled off as far as possible, and the residue dissolved in methyl alcohol. This was refluxed to destroy any remaining chromic acid, and then sufficient caustic was added to completely precipitate the chromium. The filtrate and washings were combined, treated with an excess of hydrochloric acid, and evaporated to dryness on the steam bath. The residue was then extracted with ether. The residue left after evaporation of the ether was crystallized from methanol and a melting-point determination made. The product melted at nearly the correct value for trimesic acid. A mixture of this sample with authentic trimesic acid failed to depress the melting-point. Neutral equivalent determinations gave results agreeing closely with theoretical for trimesic acid. It seems practically certain, therefore, that the identity of the hydrocarbon is established.

Summary

1. Methods have been elucidated for the preparation of

¹Kharasch and Brown, J. Am. Chem. Soc., 61, 2142 (1939).

nitro- and amino- derivatives of 1,3,5-triisopropylbenzene. These may well serve as starting materials for syntheses of other derivatives, since the amines can be diazotized and coupled.

2. Attempts to prepare 1,3,5-tri-tertiary butylbenzene have been only partially successful.

3. A discussion of steric effects in the nitration of 1,3,5-triisopropylbenzene and the possibilities of steric effects coming into play in the diazotization of 2,4,6-triisopropylaniline have been given. Extension of the same line of reasoning indicates that the possibilities are that 1,3,5-tri-tertiary butylbenzene should form only a mono-nitro derivative. That the 2,4,6-tri-isopropylphenyl radical is more strongly electronegative than the phenyl radical is indicated by the fact that 2,4,6-triisopropylaniline is a much weaker base than aniline. This view, however, does not take into account the possibility of steric hindrance factors influencing the proton-accepting ability of the amino-group.

4. Phenomena observed on the action of light upon nitro-substitution products of triisopropylbenzene have been correlated with similar observations on certain nitro-naphthalenes.

5. The following new compounds have been prepared and described: 2,4,6-triisopropyl nitrobenzene; 2,4,6-triisopropyl-1,3-dinitrobenzene; 2,4,6-triisopropylaniline, its hydrochloride, sulfate, and diazonium chloride and coupling product with beta-naphthol; 2,4,6-triisopropyl-1,3-diaminobenzene; 2,4,6-triisopropylacetanilide; and 2,4,6-triisopropyl-1,3-diacetaminobenzene.

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